Acta Cryst. (1992). C**48**, 1023–1025

Structure of Permethyltantalocenephenylmethanecarbothialdehyde Hydride, $(\eta^5\text{-}C_5Me_5)_2Ta(\eta^2\text{-}SCHCH_2C_6H_5)H$

BY JANET E. NELSON, JOHN E. BERCAW, RICHARD E. MARSH AND LAWRENCE M. HENLING

Division of Chemistry and Chemical Engineering and The Beckman Institute, Mail Code* 139-74, *California Institute of Technology, Pasadena, California* 91125, *USA*

(*Received* 13 *March* 1991; *accepted* 10 *October* 1991)

Abstract. Hydridobis(η^5-pentamethylcyclopentadienyl)(phenylmethanecarbothialdehyde-$\kappa C,\kappa S$)tantalum, $C_{28}H_{39}STa$, $M_r = 588.63$, monoclinic, $P2_1/c$, $a = 15.729\ (5)$, $b = 10.203\ (2)$, $c = 17.599\ (5)$ Å, $\beta = 116.18\ (2)°$, $V = 2535\ (1)$ Å^3, $Z = 4$, $D_x = 1.54$ g cm^{-3}; λ(Mo Kα) = 0.71073 Å, $\mu = 46.6$ cm^{-1}, $F(000) = 1184$, room temperature (297 K), $R = 0.068$ for 2333 reflections with $F_o^2 > 0$, $R = 0.054$ for 2179 with $F_o^2 > 3\sigma(F_o^2)$. The structure is disordered, with two enantiomeric molecules occupying the same crystallographic site. For the major component, the thioaldehyde ligand has an S—C bond length of 1.86 (2) Å. The ligand is bonded to the Ta center with a Ta—S bond distance of 2.418 (9) Å and a Ta—C bond distance of 2.28 (2) Å.

Introduction. Transition-metal complexes with S-containing ligands are of interest owing to their possible involvement in hydrodesulfurization reactions. While several thioaldehyde transition-metal complexes have been reported (*e.g.* Mayr, McDermott, Dorries, Holder, Fultz & Rheingold, 1986; Hofman & Werner, 1985), examples involving early transition metals are rare [Zr: Buchwald, Nielsen & Dewan (1987); Ti: Park, Henling, Schaefer & Grubbs (1990)], and hitherto no Ta complexes have been reported. We have prepared the title complex from reaction of $(\eta^5\text{-}C_5Me_5)_2Ta(\eta^2\text{-}C_6H_4)H$ and phenethyl mercaptan (phenylethanethiol). In solution, $(\eta^5\text{-}C_5Me_5)_2Ta(\eta^2\text{-}SCHCH_2C_6H_5)H$ is in rapid equilibrium with the Ta^{III} thiolate complex, which undergoes subsequent rearrangement to a permethyltantalocene sulfido alkyl species. The crystal structure of the thioaldehyde hydride complex was determined as part of the investigation of this rare example of S—C bond cleavage.

Experimental. Peach-colored crystals were grown from a concentrated THF solution cooled to 215 K. Tabular crystal fragment $0.09 \times 0.32 \times 0.52$ mm mounted in capillary with grease; space group $P2_1/c$ from photographs; CAD-4 diffractometer; cell dimensions from 24 reflections with $29 < 2\theta < 33°$. Two quadrants of data collected for $1.5 \le \theta \le 20°$, $(\sin\theta/\lambda)_{max} = 0.48$ Å^{-1}; ω scan; h from -15 to 13, k from -9 to 9, l from -16 to 16 for cell transformed after data collection. Peak broadening and substantial falloff in three standard reflections $3\bar{1}0$, $\bar{2}20$ and $1\bar{3}2$ led to rejection of final 763 of 4962 reflections measured (2345 independent). Correction for Lorentz and polarization effects; absorption correction by Gaussian integration over $8 \times 8 \times 8$ grid ($\mu r_{max} = 1.5$, transmission range 0.26 to 0.69); goodness of fit for merging 3.32 (primarily as a result of peak broadening with time, but also residual absorption effects), R_{merge} of 0.049 for 1310 reflections with exactly two observations; 12 reflections with background inconsistencies rejected. Ta atomic coordinates found by visual inspection of diffractometer intensity listing, remainder of non-H atoms by successive structure factor–Fourier calculations, S atom disordered between two sites. H atoms placed by calculation 0.95 Å from the bonded C atom with $B_{iso} = 1.2$ times the value of B_{eq} for the C atom; all methyl groups represented by six half-weight H positions, HC(1) [the H atom on the thioaldehyde C atom C(1)] disordered in conjunction with the S atom, the H atom bound to Ta obscured by disorder and subsequently ignored. Full-matrix least-squares refinement using F^2 values; variances $\sigma^2(I)$ of the individual data derived from counting statistics plus an additional term, $(0.014I)^2$, variances of the merged data by propagation of error plus an additional term, $(0.014\bar{I})^2$. H-atom parameters recalculated several times during refinement of 186 parameters including scale factor, coordinates of non-H atoms, anisotropic displacement parameters for Ta, S and methyl C atoms and isotropic for remainder, and a single population factor for the disordered pairs of atoms [refined value 0.68 (1) for S and HC(1), complementary 0.32 (1) for S′ and HC(1)′]. Final R index 0.068 for 2179 reflections with $F_o^2 > 0$, 0.054 for 1751 reflections with $F_o^2 > 3\sigma(F_o^2)$, goodness of fit = 2.55; maximum shift/e.s.d. = 0.01 in final least-squares cycle. Deviations in final

* Contribution No. 8408.

0108-2701/92/061023-03$06.00

Table 1. *Final refined parameters* ($\times 10^4$) *for* $(\eta^5\text{-}C_5Me_5)_2Ta(\eta^2\text{-}SCHCH_2C_6H_5)H$

x, y, z and $U_{eq} \times 10^4$. $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. Isotropic displacement parameters, B, are indicated by an asterisk. Populations: S, 0.68 (1); S′, 0.32 (1).

	x	y	z	U_{eq} or B
Ta	7377.0 (4)	−2109.0 (7)	7423.0 (4)	405 (2)
S	6338 (6)	−3641 (7)	7648 (6)	826 (25)
S′	8867 (11)	−3137 (15)	8521 (10)	6.1 (5)*
C(1)	7625 (14)	−3754 (19)	8374 (12)	6.3 (5)*
C(2)	7992 (18)	−5108 (26)	8377 (16)	10.6 (8)*
C(3)	7968 (15)	−6115 (19)	8987 (13)	6.3 (5)*
C(4)	8803 (18)	−6268 (24)	9750 (17)	10.5 (7)*
C(5)	8687 (20)	−7260 (25)	10333 (16)	10.7 (7)*
C(6)	7881 (21)	−7773 (25)	10008 (17)	10.4 (7)*
C(7)	7152 (22)	−7713 (29)	9324 (21)	12.7 (9)*
C(8)	7184 (19)	−6751 (26)	8789 (17)	10.9 (7)*
Cp(1)	7042 (12)	−3777 (18)	6266 (10)	4.5 (4)*
Cp(2)	8017 (11)	−3385 (16)	6590 (10)	3.9 (4)*
Cp(3)	8045 (11)	−2066 (18)	6420 (9)	4.2 (3)*
Cp(4)	7098 (12)	−1639 (16)	5952 (11)	4.7 (4)*
Cp(5)	6500 (11)	−2594 (14)	5925 (9)	3.8 (4)*
Me(1)	6637 (16)	−5103 (20)	6199 (13)	1078 (80)
Me(2)	8860 (15)	−4339 (20)	6931 (13)	1051 (71)
Me(3)	8963 (14)	−1385 (21)	6541 (13)	1011 (71)
Me(4)	6824 (15)	−388 (19)	5411 (11)	954 (74)
Me(5)	5422 (12)	−2618 (21)	5423 (12)	1093 (88)
Cp(6)	7482 (16)	190 (19)	7565 (14)	6.9 (5)*
Cp(7)	8120 (15)	−223 (18)	8394 (13)	6.3 (5)*
Cp(8)	7545 (13)	−928 (17)	8708 (12)	5.5 (4)*
Cp(9)	6651 (14)	−789 (18)	8151 (13)	6.3 (5)*
Cp(10)	6576 (14)	−100 (18)	7433 (12)	6.1 (5)*
Me(6)	7745 (32)	1279 (22)	7153 (21)	2345 (208)
Me(7)	9155 (17)	65 (27)	8816 (19)	1952 (152)
Me(8)	7997 (25)	−1400 (24)	9589 (14)	1963 (170)
Me(9)	5875 (30)	−1236 (30)	8363 (32)	3028 (186)
Me(10)	5651 (22)	423 (34)	6728 (17)	2851 (189)

Table 2. *Selected distances* (Å) *and angles* (°) *for* $(\eta^5\text{-}C_5Me_5)_2Ta(\eta^2\text{-}SCHCH_2C_6H_5)H$

Ta—C(1)	2.28 (2)	S′—C(1)	1.96 (3)
Ta—S	2.418 (9)	Ta—Cp*A**	2.156
S—C(1)	1.86 (2)	Ta—Cp*B**	2.132
Ta—S′	2.517 (17)		
C(1)—Ta—S	46.6 (5)	S′—C(1)—C(2)	86.3 (15)
Ta—S—C(1)	62.8 (7)	Cp*A**—Ta—S	104.5
S—C(1)—Ta	70.6 (7)	Cp*B**—Ta—S	104.0
C(1)—Ta—S′	47.9 (6)	Cp*A**—Ta—S′	104.4
Ta—S′—C(1)	59.7 (7)	Cp*B**—Ta—S′	101.9
S′—C(1)—Ta	72.4 (8)	Cp*A**—Ta—C(1)	115.7
Ta—C(1)—C(2)	128.5 (16)	Cp*B**—Ta—C(1)	105.1
S—C(1)—C(2)	111.2 (16)	Cp*B**—Ta—Cp*A**	139.2

* Ring centroids.

difference map from −1.7 to 2.6 e Å^{-3} near Ta; atomic scattering factors and dispersion corrections taken from Cromer & Waber (1974); programs used were those of *CRYM* (Duchamp, 1964) and *ORTEP*II (Johnson, 1976).

Discussion. Table 1 gives the final refined parameters and Table 2 gives selected distances and angles.* Figs. 1 and 2 show the molecule and the packing in the unit cell. The Ta(η^5-C_5Me_5)$_2$ geometry is unexceptional, with a ring centroid—Ta—ring centroid angle of 139.2°. An H atom and the thioaldehyde ligand are coordinated in the wedge between the rings. The S atom is in the *exo* position, with the C atom next to the hydride ligand in the wedge. Disorder results from the superposition of two enantiomers, with the thioaldehyde C atom C(1) being the asymmetric atom. The two configurations are related by the approximate interchange of the S and H positions in the wedge. The major component at each site has a population of 0.68 (1). The centrosymmetric space group produces a racemic crystal.

The bonding of the ligand to the metal center is of interest in thioaldehyde complexes. Two resonance forms have been proposed, a Ta^{III} π-thioaldehyde and a Ta^{V} thiometalacyclopropane. In this structure, the disorder affects the accuracy of the bond lengths and angles, those involving S′ (the minor site) being particularly unreliable. Nonetheless, the S—C(1) bond lengths of 1.86 (2) and 1.96 (3) Å for the major and minor components are strongly suggestive of a single bond [1.819 (19) Å for C(sp^3)—S; double bond, 1.671 (24) Å for $(X)_2$—C=S, X = C,N,O,S (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987)]. The Ta—C(1) distance of 2.28 (2) Å

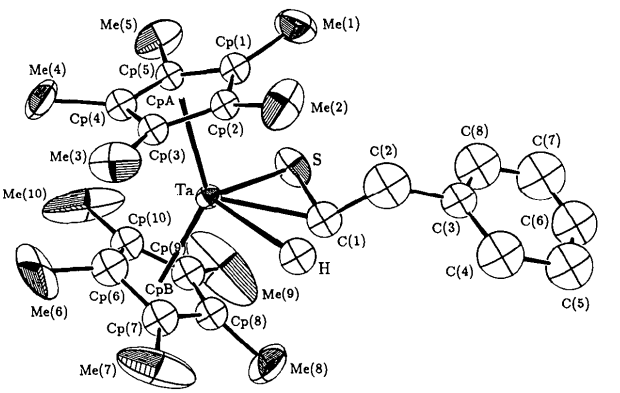

Fig. 1. An *ORTEP*II (Johnson, 1976) view of the major component with 30% probability thermal ellipsoids. The H atom bound to the Ta is at a calculated position; the remaining H atoms are not shown.

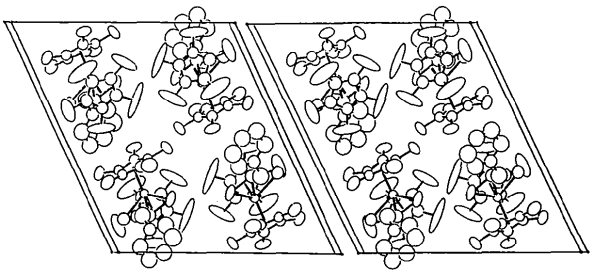

Fig. 2. A stereo *ORTEP*II (Johnson, 1976) drawing of the unit cell perpendicular to the *ac* plane. The unit cell is outlined; atoms are shown at the 30% probability level with all H atoms except the hydride omitted.

* Lists of anisotropic displacement parameters, assigned H-atom parameters, complete distances and angles, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54772 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is consistent with a single bond [2.22 (4) Å for terminal Ta—CH_3 (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989)] as are the Ta—S and Ta—S′ distances of 2.418 (9) and 2.517 (17) Å [compared to 2.529 (3) and 2.520 (3) Å for Zr—S in a zirconocene thioaldehyde complex (Buchwald, Nielsen & Dewan, 1987) and 2.452 (1) Å for Ti—S in an analogous titanocene (Park, Henling, Schaefer & Grubbs, 1990)]. Although the disorder precludes a definitive conclusion, these results suggest that the complex is primarily thiotantalacyclopropane in nature.

References

ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, p. S14.

BUCHWALD, S. L., NIELSEN, R. B. & DEWAN, J. C. (1987). *J. Am. Chem. Soc.* **109**, 1590–1591.

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

DUCHAMP, D. J. (1964). *CRYM* crystallographic computing system. Am. Crystallogr. Assoc. Meet., Bozeman, Montana. Paper B14, p.29.

HOFMAN, L. & WERNER, H. (1985). *Chem. Ber.* **118**, 4229–4238.

JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-3794, third revision. Oak Ridge National Laboratory, Tennessee, USA.

MAYR, A., MCDERMOTT, G. A., DORRIES, A. M., HOLDER, A. K., FULTZ, W. C. & RHEINGOLD, A. L. (1986). *J. Am. Chem. Soc.* **108**, 310–311.

ORPEN, A. G., BRAMMER, L., ALLEN, F. H., KENNARD, O., WATSON, D. G. & TAYLOR, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S83.

PARK, J. W., HENLING, L. M., SCHAEFER, W. P. & GRUBBS, R. H. (1990). *Organometallics*, **9**, 1650–1656.

Acta Cryst. (1992). C**48**, 1025–1027

Structure of Triaqua(nitrilotriacetato)vanadium(III) Tetrahydrate

BY KEN-ICHI OKAMOTO* AND JINSAI HIDAKA

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, *Japan*

AND MIHARU FUKAGAWA AND KAN KANAMORI*

Department of Chemistry, Faculty of Science, Toyama University, Gofuku 3190, *Toyama* 930, *Japan*

(*Received* 10 *February* 1991; *accepted* 18 *November* 1991)

Abstract. $[V(C_6H_6NO_6)(H_2O)_3].4H_2O$, $M_r = 365.17$, triclinic, $P\bar{1}$, $a = 7.929\ (2)$, $b = 8.716\ (3)$, $c = 10.914\ (3)$ Å, $\alpha = 98.77\ (2)$, $\beta = 90.30\ (2)$, $\gamma = 105.79\ (2)°$, $V = 716.4\ (8)$ Å^3, $Z = 2$, $D_x = 1.693$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 7.3$ cm^{-1}, $F(000) = 380$, room temperature. $R = 0.060$ for 3829 independent reflections [$F_o > 3\sigma(F_o)$]. The V atom is surrounded by three O atoms of the water molecules, and one N and three O donor atoms of the title ligand (nta). The geometry is described as a capped octahedral seven-coordinate structure. Two triangular faces consist of three O atoms of the nta ligand and three water molecules respectively, and they are almost parallel. The N donor atom is placed on the triangular face formed by three O atoms of the nta ligand.

Introduction. Recently vanadium(III) chemistry has attracted much attention, especially in relation to the status of vanadium in ascidians (Michibata & Sakurai, 1990). A V^{III} complex with a nitrilotriacetate (nta) ligand was first prepared by Podlaha & Petras (1970), and formulated as $[V(nta)(H_2O)_2].5H_2O$. They reported that the complex is fairly resistant to air oxidation, though V^{III} complexes, in general, are quite air sensitive. In order to establish the geometry of the air-stable V^{III}–nta complex, we have determined its crystal structure.

Experimental. All procedures in the sample preparation were carried out under an argon atmosphere by using a standard syringe and vacuum-line techniques. The title complex was prepared as follows: $V_2(SO_4)_3$ (3.9 g) (Claunch & Jones, 1963) was suspended in 50 cm^3 of water. The suspension was stirred at 333 K for 2 d to give a brownish green solution. The mixture of H_3nta (3.8 g) and $BaCO_3$ (5.3 g) in 50 cm^3 of water was added to the above V^{III} solution. By stirring at 313 K for 1 d, a green solution with a white precipitate of $BaSO_4$ was obtained. The precipitate was filtered off and the filtrate reduced to half the volume. The solution was allowed to stand in an ice bath for several hours. The green crystals which appeared were collected by filtration, washed with a

* To whom correspondence should be addressed.

0108-2701/92/061025-03$06.00